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Light Scattering from Polymer Blend Solutions. 6. Temperature Dependence of Interaction Parmeter

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Dilute bromobenzene solutions of polymer blends polystyrene/poly(methyl methacrylate), polystyrene/polyisoprene and polystyrene/polyisobutylene were studied by light scattering under an "optical θ" condition, and the polymer-polymer interaction parameter χ_{12} was evaluated as a function of temperature. The segment-segment interaction parameter χ_{12}^{o} estimated on the basis of the χ_{12} and other information was found to decrease with an increase of temperature in all the systems, indicating a USCT behavior in the bulk in the studied temperature range (from about 20°C to about 80°C).

KEY WORDS: Polymer-polymer interaction parameter/Compatibility/Excluded volume effect/UCST/

INTRODUCTION

In previous papers[1-3], we have studied dilute solutions of some polymer blends by means of light scattering carried out under the special condition termed "optical θ". This method has proved to allow much more precise determination of the *polymer-polymer* interaction parameter χ_{12}[4] than the classical method.[5] On the basis of this phenomenological parameter and other information, we have estimated the *segment-segment* interaction parameter χ_{12}^{o} by the aid of the excluded-volume theory.[6] This "molecular" parameter χ_{12}^{o} was found to be in fact independent basically of molecular weight, blend composition and solvent, and rather similar in value to the corresponding parameter for the bulk systems (see Ref. 7 for a review).

The purpose of this paper is to study the temperature dependence of the parameters χ_{12} and χ_{12}^{o} for the same systems. Our central interest is to predict through χ_{12}^{o} the behavior of the dry blends, e.g., upper critical- versus lower critical solution temperature behavior (UCST vs. LCST). We compare results with corresponding data for the bulk systems, whenever such are available.

EXPERIMENTAL

The molecular characteristics of samples of polystyrene (PS), poly(methyl methacrylate) (PMMA), polyisoprene (PIP) and polyisobutylene (PIB) are listed in Table I. All the

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Table I Characteristics of Polymer Samples.

Polymer	Code	$10^{-4}M_w$[a]	M_w/M_n[b]
PS	PC200'[c]	183 (179)	1.30
PS	S 50[d]	51.0 (51.5)	1.03
PS	F10[e]	(10.2)	(1.02)
PMMA	75M[f]	214	1.35
PIB	B50[g,h]	54.3	1.43
PIP	I13[h]	(14.3)	(1.04)

a) Determined by light scattering (nominal value is in parentheses).
b) Determined by GPC (nominal value is in parentheses).
c) Pressure Chemicals Co. d) Showa Denko Co.
e) Toyo Soda Co. f) See Ref. 1. g) Fraction of a commercial polymer. h) Polymer Laboratories Co.

samples have a narrow or reasonably narrow distribution in molecular weight (for the sample sources, see the footnotes for Table I). The volume fraction ϕ_i and the degree of chain length m_i of polymer i (=1 or 2) were calculated with

$$\phi_i = w_i v_i / (w_0 v_0 + w_1 v_1 + w_2 v_2) \quad (1)$$

$$m_i = M_{i,w} v_i / V_0 \quad (2)$$

Here w_i is the weight fraction, v_i is the specific volume in the pure state, $M_{i,w}$ is the weight-average molecular weight, and V_0 is the molar volume of solvent (i=0, 1 or 2 with 0 denoting the solvent and thus m_0=1). The values of v_1 and v_2 were assumed to be given by the following relations determined for the liquid polymers:

$$v_1 = 0.9199 + (5.08 + 2.354 \times 10^{-3} t) \times 10^{-4} t \quad \text{(PS)}^{8)}$$

$$v_2 = 0.9096 + 5.04 \times 10^{-4} t \quad \text{(PMMA)}^{9)}$$

$$= 1.080 + 6.89 \times 10^{-4} t \quad \text{(PIP)}^{10)}$$

$$= 1.077 + 6.45 \times 10^{-4} t \quad \text{(PIB)}^{11)}$$

where t is the temperature in °C

The refractive index increment of the polymers in bromobenzene were determined on a Union Giken differential refractometer Model RM102, Japan. The following relations were found for the temperature range 20°C$\leqq t \leqq$60°C.

$$\partial n/\partial c = 0.039_6 + 3.1_0 \times 10^{-4} t \quad \text{(PS)}$$

$$= -0.059_6 + 3.3_5 \times 10^{-4} t \quad \text{(PMMA)}$$

$$= -0.053_3 + 2.7_0 \times 10^{-4} t \quad \text{(PIP)}$$

$$= -0.082_3 + 3.8_0 \times 10^{-4} t \quad \text{(PIB)}$$

where c is polymer concentration in g mL^{-1}. These relations are assumed to be valid even for temperatures somewhat higher than 60°C, because precise determination of $\partial n/\partial c$ was difficult for that temperature renge.

Light scattering reasurements were made on a Fica light scattering photometer Model 50, France, by using a vertically polarized light of 436 nm. Each solution was composed of

Table II Light Scattering Results for PS/PMMA, PS/PIB and PS/PIP in Bromobenzene at Several Temperatures.

Polym.-1	Polym.-2	t (°C)	$[\eta_1]$ (dL g^{-1})	$[\eta_2]$ (dL g^{-1})	χ_{12}	χ_{12}^{o}
PS PC2000′	PMMA 75M	15	4.19	2.93	0.0029	0.041
		30				0.031 [a]
		60	4.12	3.23	0.0028	0.038
		90	4.07	3.43	0.0023	0.030
PS S50	PIB B50	30				0.428 [b]
		50	1.65	1.29	0.0224	0.301
		70	1.63	1.54	0.0194	0.226
PS F10	PIP I13	20	0.48	0.98	0.0189	0.124
		30				0.149 [b]
		60	0.48	1.03	0.0134	0.077
		90	0.48	1.06	0.0119	0.064

a) Average value from Ref. 6. b) Average value from Ref. 3.

a PS and one of the other polymers of a similar molecular weight, blended in such a ratio as to meet the optical θ condition represented by eq. (3) at each temperature:

$$\psi_1 m_1 x_1 + \psi_2 m_2 x_2 = 0 \qquad (3)$$

where $\psi_i = \partial n/\partial \phi_i = (\partial n/\partial c_i)/v_i$, and $x_i = \phi_i/\phi$ with $\phi = \phi_1 + \phi_2$ being the total concencentration of polymers.

The intrinsic viscosioy $[\eta]$ of each polymer in bromobenzene was determined at the relevant temperatures. The hydrodynamic expansion factor α_η is evaluated by

$$\alpha_\eta^3 = [\eta]/K_0 M_w^{1/2} \qquad (4)$$

with values of K_0 (in mLg^{-1}) of 0.079 for PS, 0.049 for PMMA, 0.097 for PIP and 0.112 for PIB.[3] The temperature dependence of K_0 is small enough to be neglected for the present purpose. Then, α_η is used to evaluate the excluded-volume parameter Z according to the semiempirical relation[12]

$$\alpha_\eta^4 = 1 + (7/5)Z \qquad (5)$$

Thus-estimated Z is used to estimate, on the basis of the theories[6], the mean-square radius $<S^2>$ and other parameter values necessary for later analysis. Values of $[\eta]$ are listed in Table II.

RESULTS AND DISCUSSION

When the condition in eq. (3) is met, the forward scattering intensity R_0 can be represented simply by[1-3]

$$K\phi/R_0 = (m_1 x_1)^{-1} + (m_2 x_2)^{-1} - 2x_{12}\phi + \cdots \qquad (6)$$

where K is a constant proportional to $(\psi_1 - \psi_2)^2$. Thus the parameter χ_{12} is determined from

the initial slope of the $K\phi/R_0$ vs. ϕ plot without regard to the solvent-polymer interactions.

Figures 1-3 show the plot experimentally obtained. Values of R_0 were determined by the conventional angular extrapolation method of Zimm. In all cases, the plot gives a well-defined initial slope. Values of χ_{12} are listed in Table II.

In each system, χ_{12} is positive and decreases with increasing temperature. From this result, one would expect that compatibility in these systems in imporved by raising the temperature. This is presumably correct but not conclusively, because χ_{12} is merely a phenomenological parameter akin to the excess second virial coefficient ΔB[13], which reflects not only the degree of compatibility or incompatibility of the parent polymers but also the excluded volume effect between them. We have discussed this matter in a previous paper, wherein χ_{12} was given in the form

$$\chi_{12}=(1-\chi_{01}^{0}-\chi_{02}^{0}+\chi_{12}^{0})h_0(\bar{Z}_{12}) -(1/2)[(1-2\chi_{01}^{0})h_0(\bar{Z}_{11})+(1-2\chi_{02}^{0})h_0(\bar{Z}_{22})] \quad (7)$$

Here $h_0(\bar{Z}_{ij})$ is the function, appearing in the theory of the second virial coefficient[14], that describes the excluded volume effect between *molecules* i and j ($=1$ or 2), and χ_{ij}^{0}

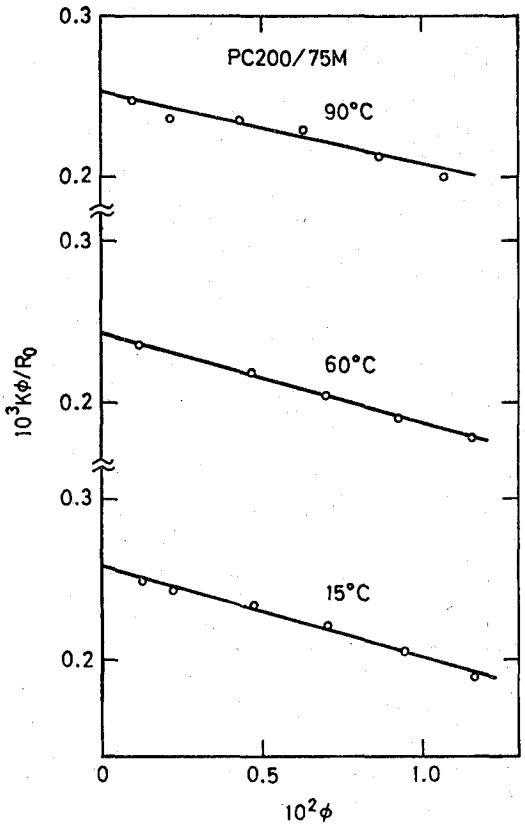

Fig. 1. Plot of K/R_0 vs. ϕ for PS/PMMA/bomobenzene solutions under optical θ conditions.

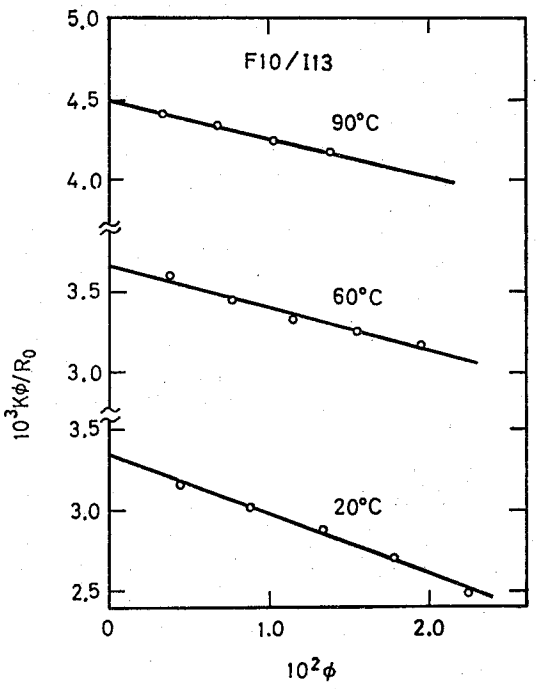

Fig. 2. Plot of $K\phi/R_0$ vs. ϕ for PS/PIP/bromobenzene solutions under optical θ conditions.

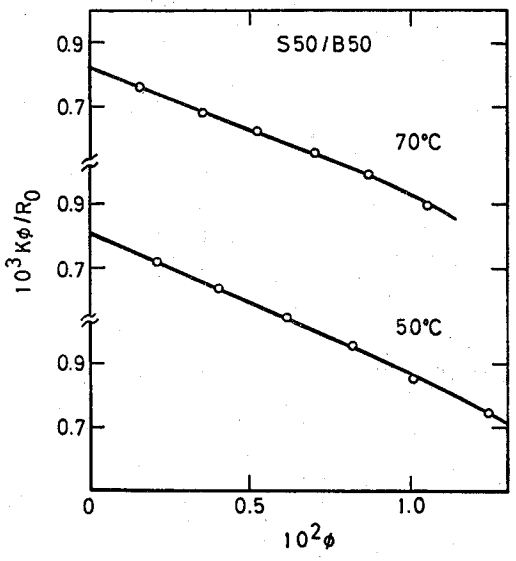

Fig. 3 Plot of $K\phi/R_0$ vs. ϕ for PS/PIB/bromobenzene solutions under optical θ conditions.

characterizes the interaction between segments i and j (0, 1 or 2). On the basis of the equations of $\bar{Z}_{12}$ and h_0 proposed in Ref. 6, eq. 7 can be numerically solved for χ_{12}° provided that values of χ_{12}, χ_{0i}° and $<S_i^2>$ are known (for the latter two quantities, see the section under *Experimental*). Values of χ_{12}° thus estimated are given in Table II.

Figure 4 shows χ_{12}° as a function of inverse temperature. In each system, χ_{12}° decreases with increasing temperature, indicating a UCST behavior in the bulk system. In the examined temperature range, the PS/PIB system has the largest χ_{12}° and the largest dependence on temperature, while the PS/PMMA system is the smallest in both respects.

As to PS/PIP, Mori, Hasegawa and Hashimoto[15] recently studied the X-ray scattering from a dry, disordered PS-PIP block copolymer to determine χ_{12} as a function of temperature. Part of their result is indicated by the broken curve in Figure 4, to which our χ_{12}° data are rather close. Benoit et al.[16] have studied a blcok copolymer of PS-PMMA type by neutron scattering and suggested a χ_{12} value about 0.005 at 160°C. This value seems to be, though not in close agreement, compatible in the order of magnitude with the value about 0.02 expected from our data for that temperature. Koningsveld and Kleintjens[17] have studied the phase behavior of a low-molecular weight blend of PS/PIB in bulk. They observed strong composition dependence of the interaction parameter g_{12}[17,18] in their system. For this reason, comparison of the solution- and the bulk data would make no strict sense. We only note that our χ_{12}° is generally comparable in the order of magnitude with their g_{12}, but that in the light of their result, the temperature dependence of our χ_{12}° seems somewhat unreasonably large.

In conclusion, dilute solutions of a polymer blend provide at least semi-quantitative information on compatibility behavior of the polymers in bulk.

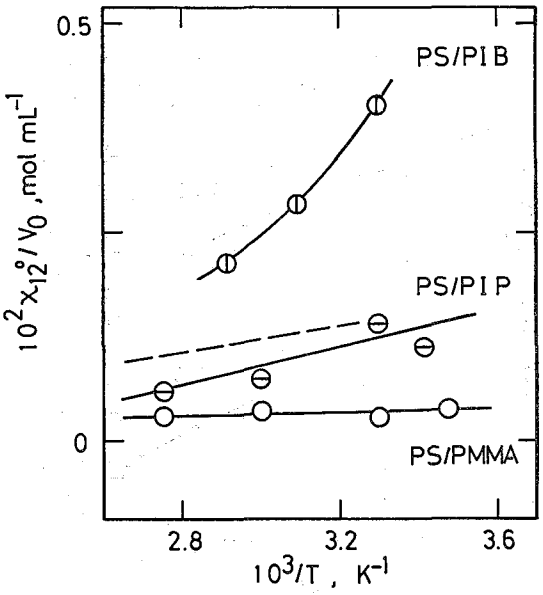

Fig. 4. Values of χ_{12}°/V_0 as a function of inverse temperature: V_0 is the molar volume of solvent (or segment) in mL/mol, and the broken curve shows part of the χ_{12} bata for a dry PS-PIP block copolymer from Ref. 15.

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